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(54) Alcohol Purification

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PATENT APPLICATION OF

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for

ALCOHOL PURIFICATION

Abstract of the Disclosure

A method for purification of a lower alkanol containing corrosion-producing impurities selected from organic acids and metal salts by contacting the alkanol with two or more ion exchange resins, at least one of which is a cation exchange resin and another of which is an anion exchange resin.

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BACKGROUND OF THE INVENTION

This invention is related to the purification of alcohols and the alcohols so purified and is particularly directed to those alcohols used as fuels or fuel additives in internal combustion engines.

Alcohols such as methanol, ethanol and also higher alcohols are used as fuels or fuel additives for internal combustion engines, but it has been found that certain problems are associated with such use. One particular problem is the corrosion of metal parts from the fuel tank to and including the carburetor when such alcohols are used. Such corrosion is presently a very serious problem with alcohol-fueled automobiles, trucks and buses being manufactured and sold in Brazil where the alcohol (ethanol) used is obtained by fermentation of biomass; e.g., cellulose and the like. Although the alcohol obtained from biomass fermentation is distilled and may be otherwise highly purified prior to use as a fuel, the corrosion problem persists and parts



replacement, particularly of carburetor parts, is necessary after only several thousand miles of travel. Obviously, there is a need to alleviate or eliminate this serious problem. Reference is made to
5 the Proceedings Fifth International Alcohol Fuel Technology Symposium, Volume II, Auckland, New Zealand, May 13-18, 1982, where these corrosion problems are discussed.

It has now been found that the corrosion problem
10 associated with alcohol fuels and alcohol fuel additives can be remarkably reduced or even eliminated by subjecting the alcohol to a specific purification process for removal of even extremely small amounts (parts per million) of the impurities which appear to
15 cause the corrosion. Thus, by means of this invention, corrosion-free alcohol fuels and fuel additives can be obtained and a process is provided for obtaining such products. Furthermore, this is accomplished without otherwise changing the suitability of the alcohol for
20 use as a fuel or fuel additive. The process of this invention may also be employed for the purification of alcohols derived from sources other than fermentation; e.g., ethanol from hydration of ethylene, alcohols from
25 natural gas or coal and the like.

BRIEF STATEMENT OF THE INVENTION

In accord with the invention, alcohols are
30 purified to remove corrosion-causing contaminants by contacting the alcohol with particles of two specific, oppositely charged ion exchange resins, one resin being a strongly or weakly acidic cation resin and the second being a strongly or weakly basic anion exchange

resin. It is believed that the process of the invention effectively removes the organic acids (e.g., acetic acid) and metal salts (e.g., chlorides, sulfates, and nitrates and the various metal counterions, e.g., copper, sodium, iron, calcium, magnesium, etc.) which are responsible for the corrosion.

The present invention, in one aspect, resides in a method for purification of a fermentation-derived, hydrated ethanol which is to be used as a fuel for motor vehicles, said hydrated ethanol containing corrosion-producing impurities, which method comprises contacting said ethanol containing said impurities with two or more ion exchange resins, at least one of which is a cation exchange resin and another of which is an anion exchange resin whereby the impurities are substantially removed from said ethanol.

The present invention additionally provides a method for removing corrosion-producing impurities from a fermentation-derived hydrated ethanol which is to be used as a fuel for motor vehicles, which method comprises passing said ethanol at a flow rate of about 1 to about 20 bed volumes per hour, first through a bed of either a strongly basic anion exchange resin or a strongly acidic cation exchange resin and thereafter through a bed of oppositely charged ion exchange resin.

In another aspect, the present invention resides in corrosion-free fermentation-derived, hydrated ethanol fuel or fuel additive containing less than 5 ppm of organic acids and less than 1 ppm of metal salts.

The present invention, in a further aspect, resides in corrosion-free, fermentation-derived, hydrated ethanol fuel or fuel additive which has been treated with a strongly basic anion exchange resin and a strongly acidic cation exchange resin to reduce the organic acid content of said hydrated ethanol to less than 5 ppm and the metal salts content of said hydrated ethanol to less than 1 ppm.

It is surprising that the strongly basic anion exchange resins of the type described elsewhere herein have much greater capacity for removing the organic acids than the weakly basic resins which are known in the art as excellent acid scavengers. To remove significant amounts of both cations and anions contributed by the metal salt impurities, the initial contact between the alcohol and ion exchange resin should be conducted with a strongly acidic or strongly basic resin, preferably the former, or alternatively both, to achieve salt-splitting. Otherwise, the desired result of removing the metal and its counterion may not be fully achieved.

The cation and anion exchange resins are normally used in the form of stationary "beds" or "columns" through which the impure alcohol is circulated either upflow or downflow as desired. Alternatively, the present process can be operated in a so-called "mixed bed", that is, a bed containing a physical mixture of both cation and anion exchange particles. High levels of purification are desirably achieved using separate cation and anion beds in series flow followed by a mixed bed which serves as a "polisher".

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DETAILED DISCUSSION OF THE INVENTION

In carrying out the process of the invention, the alcohol is contacted with a first resin which is a cation exchange resin, preferably a strongly acidic cation exchange resin containing sulfonic acid functionality. Typical resins of this type which may be used are the "Amberlite®" resins manufactured by Rohm and Haas Company and equivalent resins. Prior to use in the process these resins will be put in the acid (hydrogen ion) form. It is believed that in contacting the alcohol, these resins adsorb the small amounts of cation contaminants in the alcohol. Macroreticular, gel-type, or other type resins may be used.

The second resin required in the process will be a strongly basic anion exchange resin having quaternary ammonium functionality or a weakly basic resin containing some strong base active sites. These resins remove the acids (e.g., acetic acid) which are in the alcohol and which contribute to the corrosion problem and the mineral acids formed from the salt-splitting reaction when the alcohol is first treated with a strongly acidic resin. Here again, macroreticular, gel-type or other type resins may be employed.

Both cation and anion exchange resins useful for the present invention are known to the art. Methods for preparing such resins in both gellular and macroreticular form are disclosed in prior patents and other publications, e.g., U.S. Patent 4,382,124 of E.F. Meitzner and J.A. Oline, issued May 3, 1983. Weakly basic resins have predominantly a weak base functional moiety, such as an amine group,

but can contain also a minor amount of a strongly basic functional moiety, such as a quaternary ammonium group. The strongly acidic and weakly acidic resins contain, respectively, sulfonic acid functionality and
5 carboxylic functionality.

Preferably, the process of the invention can be conducted by passing the alcohol to be treated through a separate bed of each resin, normally, first through a bed of the cation exchange resin and then through a bed
10 of the anion exchanger. However, flow through the anion resin first and then the cation resin is also operable. The rate of flow of the alcohol to be treated may vary over a wide range and will, to a large extent, be dictated by the concentration of impurities
15 in the alcohol. In general, however, flow rates of from about 1 to about 20 bed volumes per hour (BV/hr) will be suitable for purification, with from about 2 to about 16 BV/hr preferred.

Although a dual bed system as described above is
20 preferred, the process may be operated in the Rohm and Haas Monobed® system mode; i.e., where the anion exchange resin and the cation exchange resin are physically intermixed and used as a single bed.

It is also possible to obtain some purification of
25 the contaminated alcohol by subjecting it to treatment with a single ion exchange resin. In such a procedure it is preferred to use a strongly basic ion exchange resin, generally having quaternary ammonium functionality, of the styrene-divinylbenzene type. It
30 will be understood that use of a single resin, while effecting some purification of the alcohol in removing the corrosive materials present, is not a preferred procedure.

It will also be understood that each of the resins may be regenerated after they have reached their capacity for effective removal of contaminants.

Regeneration of these resins is, of course, well-known in the art and involves removal of the adsorbed and absorbed moieties by use of appropriate regenerants to restore the cation exchange resin to the acid form and the basic resin to the free base or hydroxide form for weakly basic or strongly basic resin, respectively.

Typically the anion exchange resin may be eluted with a 4% aqueous sodium hydroxide solution and the cationic resin with aqueous sulfuric or hydrochloric acid for regeneration. Other reagents and methods of regeneration are well known.

The process of the invention will generally be operated at ambient temperature and atmospheric pressure. It is important only to keep the temperature below the decomposition point of the resin and below the boiling point of the alcohol.

The alcohols to be treated by the process will, as indicated, be preferably those used as fuels or additives for fuels for internal combustion engines. Such alcohols include the lower alkanols containing from one to about six carbon atoms. Vehicles fueled entirely with hydrated ethanol are in use in large numbers in Brazil and some using methanol are also being used in other localities. Methanol also is a useful fuel additive as are isopropanol, the isomeric butanols, pentanols and the like. Methanol made from natural gas, coal or other sources and other alcohols made by fermentation, oxidation and other processes will often be hydrated and contain many of the impurities removable by the process of this

invention. Such impurities, believed to comprise acids (formic, acetic, etc.), metal salts of chlorides, sulfates, nitrates and the like are believed to be responsible for the corrosion effects in fuel tanks, fuel lines, and particularly, fuel pumps and carburetors. These impurities are generally present in amounts of 10 to 100 ppm, more frequently 25 to 50 ppm, and are readily removed by the process of this invention to below a level of 1 ppm. However, off-grade alcohols will contain larger amounts of acid and other impurities and also may be treated by the process of the invention. Thus, for example, certain off-grade fermentation ethanol containing from about 400 to about 20,000 ppm of acetic acid is often available and may be treated by this invention to remove the acid contamination. Thus, the ion exchange resins used in accord with this invention can be used in two distinct areas for purification of alcohol: 1) High acidity alcohol, up to at least 10,000 ppm, can be reworked without costly distillation to levels of 0.5-5 ppm of total acidity with complete removal of metal sulfates and chlorides within the limits of detection by analytical methods, 2) Normal hydrated alcohol for automobiles of 30-45 ppm acidity can be treated to give an alcohol of 0.5-5 ppm total acidity, again without chlorides and sulfates. Thus, the problems observed with acid containing alcohols, particularly in alcohol-fueled vehicles may be reduced or totally eliminated by the process of this invention.

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EXAMPLESExample 1

5 A synthetic mixture of ethanol (95% by volume ethanol, remainder water and impurities) and various corrosive additives was diluted to give a mixture as follows:

	Ethanol	≈90% by volume
	Water	≈10% by volume
10	Acetic acid	30 ppm
	NaCl	2 ppm
	NaNO ₃	2 ppm
	Na ₂ SO ₄	8 ppm

15 The above alcohol mixture was first passed through a bed of strongly acidic cation exchange resin in the hydrogen form to convert the salts to their corresponding acids before being passed through an anion exchange resin. The resin beds were prepared
20 using 50 mls of resin in 1/2" (I.D.) glass columns. The column elutions were run at 2 BV/hr and samples titrated to the Bromothymol blue end point with standardized 0.01 N NaOH.

25 The data for runs through two weakly basic and one strongly basic anion exchange resin are summarized in Tables 1, 2 and 3 below.

As can be seen from the data in Tables 1, 2 and 3, there is a breakthrough in total acidity in the elutant at about 234 bed volumes for weakly basic resins, resin
30 ALA-50 (Table 1) and at about 182 bed volumes for resin ALA-60 (Table 2), whereas, with strongly basic resin ALA-20 (Table 3) the breakthrough point is at about 674

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bed volumes, thus clearly establishing surprising
superiority for removal of acetate ions. It was also
observed that with the strongly basic resin no acids
developed in the purified alcohol after three months'
5 storage at room temperature, thus showing the permanent
effects of the purification process.

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Table 3
Amberlite ALA-20 Resin¹¹¹
Total Acidity
BV ppm as Acetic Acid

12	4.1
155	3.8
180	3.5
196	3.5
211	2.9
226	3.4
248	3.5
260	2.9
320	2.9
400	2.9
470	2.9
485	4.1
559	4.1
563	5.3
609	5.3
664	5.3
669	7.6
674	10.6
679	12.4
684	15.3
718	18.9
732	22.7
753	23.6
773	26.5
780	28.9
800	31.8
810	35.6
820	38.6
858	39.5
868	42.4
878	43.9

Table 2
Amberlite ALA-60 Resin¹¹
Total Acidity
BV ppm as Acetic Acid

4	0
50	2.9
101	4.1
134	4.6
158	6.8
170	9.4
182	13.2
201	18.0
210	21.5
226	25.6
249	28.4
304	31.2

Table 1
"Amberlite" ALA-50 Resin¹
Total Acidity
BV ppm as Acetic Acid

8	3.5
179	3.5
223	4.4
234	11.2
254	14.7
262	22.5
266	30.5
270	37.9
280	40.6
285	43.0

- 5
- 10
- 15
- 1 ALA-50 resin is a macroreticular, weakly basic anion exchange resin of the styrene-divinylbenzene-polyamine functionality type.
- 20
- 25
- 11 ALA-60 resin is a weakly basic gel type anion exchange resin (polyamine functionality) of the acrylic-divinylbenzene type.
- 30
- 111 ALA-20 resin is a macroreticular strongly basic anion exchange resin (quaternary ammonium functionality) of the styrene-divinylbenzene type.
- 35

("Amberlite" is a trademark)

Example 2

Three additional strongly basic Amberlite anionic exchange resins were evaluated at a higher flow rate (16 BV/hr) using the alcohol mixture of Example 1.

- 5 Table 4 shows the data obtained and that breakthrough with resin ALA-10 was at about 1370 bed volumes, with resin ALA-40 at about 1000 bed volumes and with resin ALA-30 at about 1350 bed volumes. Comparing these data with that of Table 1 shows the very high efficacy of
- 10 the preferred resins used in the invention.

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TABLE 4
Evaluation of Strongly Basic Resins at 16 BV/hr

		<u>Total Acidity - ppm as Acetic Acid</u>		
	<u>BV</u>	<u>ALA-10^(a)</u>	<u>ALA-40^(b)</u>	<u>ALA-30^(c)</u>
5	50	0.6	0.6	0.6
	100	1.2	1.2	1.2
	150	2.4	1.5	1.8
	200	2.1	2.1	2.1
	300	2.1	2.1	2.1
10	400	2.1	2.1	2.1
	500	2.4	2.1	2.4
	600	2.4	2.1	2.1
	700	2.1	2.1	2.1
	800	2.1	2.4	2.4
15	900	2.4	3.5	2.4
	950	2.4	5.6	2.4
	1000	2.4	13.6	2.4
	1050	2.4	28.0	2.4
	1100	2.4	34.8	2.4
20	1150	2.4	38.9	2.4
	1300	4.1	-	2.9
	1350	9.7	-	10.0
	1370	15.9	-	17.4
	1390	25.3	-	27.4
25	1410	34.2	-	32.4

a Acrylic gel type resin with quaternary ammonium functionality

b Macroreticular acrylic type resin with quaternary ammonium functionality

c Macroreticular styrene type resin with quaternary ammonium functionality

Example 3

This example demonstrates that high concentrations of acetic acid can be removed from ethanol by the method of the invention. An influent stream of 10,000 ppm acetic acid was successfully treated with "Amberlite ALA-20".* The same ALA-20 resin was regenerated with 4% NaOH, and a series of five exhaustion/regeneration cycles was successfully carried out with the 10,000 ppm acetic acid influent.

10 The details follow:

A sample of 90% undenatured alcohol which was spiked with 10,000 ppm acetic acid was prepared in the laboratory. This alcohol was passed through a 50 ml bed of "Amberlite ALA-20" in a 1/2" I.D. glass column at 2 BV/hr. Breakthrough was selected as occurring at 10 ppm which represented essentially complete utilization of the capacity for the ALA-20 resin. The resin was regenerated at 200% of theory with 4% NaOH at a flow rate of 1 BV/hr. The resin was then slow rinsed with distilled H₂O at 2 BV/hr for one hour and then fast rinsed at 16 BV/hr for thirty minutes. A final rinse with 90% ethanol (no acetic acid) at 2 BV/hr for one hour was carried out before proceeding to a second exhaustion cycle with the 10,000 ppm acetic acid influent. The exhaustion/regeneration cycles were run for a total of 5 cycles. After the initial experiment which resulted in virtually complete utilization of resin capacity, the capacity dropped from an initial 1.0 meg/ml to a relatively constant value of 0.88 meg/ml wet (using 10 ppm as the breakthrough point). It may be concluded from these data that "Amberlite ALA-20" can successfully deacidify a 90% ethanol stream

* Trademark



containing at least 10,000 ppm acetic acid and that the ALA-20 can be successfully regenerated with 4% NaOH.

Example 4

This example illustrates the purification of
5 actual Brazilian fuel alcohol. A 50 ml bed of
Amberlite ALA-20 was utilized to deacidify the Brazil
alcohol at a flow rate of 8 BV/hr. The results are
summarized in Table 5. The elution was limited to
200 BV due to a lack of sufficient alcohol to run to
10 the breakthrough point. Although the Brazilian alcohol
used in this study contained only 15 ppm acetic acid,
the column effluent was a very consistent 1.5 ppm. It
should be noted that this Brazil alcohol sample was
apparently contaminated with what is believed to be
15 gasoline (based on odor and mass spectrometry data) and
when permitted to evaporate, a very oily residue was
observed.

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Table 5
Deacidification of Brazilian Alcohol
Containing 15 ppm Acetic Acid
Resin: ALA-20 at 8 BV/hr

	<u>Bed Volume</u>	<u>ppm Total Acidity as Acetic Acid</u>
5	5 thru 8	1.5
	13 thru 16	1.5
	21 thru 24	1.5
	29 thru 32	1.5
10	37 thru 40	1.5
	73 thru 76	1.5
	105 thru 108	1.5
	125 thru 128	1.5
	157 thru 160	1.5
15	192 thru 200	1.5

Example 5

Table 6 shows the results of treating a distilled Brazilian alcohol containing 12 ppm of acetic acid with 20 Amberlite ALA-20. As can be seen, effective removal of acid occurs for at least 1500 bed volumes before breakthrough.

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Table 6
Low Acidity Alcohol
Treated with ALA-20

	<u>BV</u>	<u>In</u>	<u>Out</u>
5	10	12	4.5*
	40	12	4.5*
	100	12	4.5*
	200	12	4.5*
	350	12	4.5*
10	550	12	4.5*
	750	12	4.5*
	1000	12	4.5*
	1300	12	4.5*
	1500	12	4.5*
15	1700	12	10.5

* Due to the lack of accuracy of the analytical equipment utilized, this number is believed to be higher than actual and probably should be in the 1.5-3 ppm range.

Example 6

As in Example 5, a distilled Brazilian alcohol high in acidity was treated with Amberlite ALA-20. The input alcohol contained 45.3 ppm of chloride ion and 80 ppm of sulfate ion, but after passing through the resin at 5 BV, analysis showed that the alcohol contained neither chloride nor sulfate. Several analyses by various methods also showed the input alcohol under test to contain on average about 1100 ppm of acetic acid acidity, but after passing through the resin at 5 BV, acidity was reduced to a level of about

10 ppm.

Example 7:

Corrosion tests were conducted with Brazilian alcohol fuel which indicated a significant difference between treated and untreated alcohol over a 60-day test period, the alcohol treated with ion exchange resin showing much less corrosion on carbon steel test panels immersed in the alcohol samples. Over a 183-day test period the advantage for the treated alcohol was still evident, but less so than in the 60-day test. After 225 days of test, no significant difference between the samples was observed. However, it must be understood that an immersion test of this type does not represent the conditions under actual use; i.e., in use as fuel in a vehicle fresh alcohol flows through the system and is unlike the static test conditions. The 60- to 183-day test results are believed to be meaningful in indicating the significant beneficial results achieved with alcohol treated by the process of the invention.

It is evident from the above description of the invention and the data obtained that the method of the invention enables the corrosive elements to be removed from fuel and fuel additive alcohols and that the process represents a significant contribution to the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for purification of a fermentation-derived, hydrated ethanol which is to be used as a fuel for motor vehicles, said hydrated ethanol containing corrosion-producing impurities, which method comprises contacting said ethanol containing said impurities with two or more ion exchange resins, at least one of which is a cation exchange resin and another of which is an anion exchange resin whereby the impurities are substantially removed from said ethanol.

2. The method of claim 1 wherein the ethanol is passed first through a bed of either a strongly basic anion exchange resin or a strongly acidic cation exchange resin, and thereafter through a bed of oppositely charged ion exchange resin.

3. The method of claim 1 wherein said cation exchange resin and said anion exchange resin are intermixed in a single bed.

4. A method for removing corrosion-producing impurities from a fermentation-derived hydrated ethanol which is to be used as a fuel for motor vehicles, which method comprises passing said ethanol at a flow rate of about 1 to about 20 bed volumes per hour, first through a bed of either a strongly basic anion exchange resin or a strongly acidic cation exchange resin and thereafter through a bed of oppositely charged ion exchanged resin.

5. Corrosion-free, fermentation-derived, hydrated ethanol fuel or fuel additive containing less than 5 ppm of organic acids and less than 1 ppm of metal salts.

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6. Corrosion-free, fermentation-derived, hydrated ethanol fuel or fuel additive which has been treated with a strongly basic anion exchange resin and a strongly acidic cation exchange resin to reduce the organic acid content of said hydrated ethanol to less than 5 ppm and the metal salts content of said hydrated ethanol to less than 1 ppm.



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REMPLACEMENT

SECTION is not Present

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